ZEOLITES: RAW MATERIAL FOR CERAMIC PIGMENTS

V. M. Pogrebenkov,[1] M. B. Sedel'nikova,[1] and V. I. Vereshchagin[1]

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The possibilities of using natural zeolite for synthesizing ceramic pigments are investigated. The special features of isomorphism of bi- and trivalent cations in the zeolite lattice are analyzed. It is shown that it is possible to obtain pigments with the structure of anorthite and mullite using a zeolite structure with additives (alumina, wollastonite).

Ceramic pigments are based on the crystal structures of minerals obtained by high-temperature synthesis from pure chemical substances. There are published data on the use of natural minerals for creating ceramic pigments [1]. Silicates attract special interest due to their capacity for isomorphism and good ion-exchange properties.

Zeolites, i.e., aluminosilicates with a skeleton structure, possess exceptional susceptibility to isomorphism. The primary element of the zeolite skeleton is a tetrahedron with the center occupied by a silicon or an aluminum atom and four oxygen atoms positioned in the vertices. Each oxygen atom is a common element for two tetrahedrons. The set of all tetrahedrons forms a continuous skeleton. The replacement of Si^{4+} by Al^{3+} in the tetrahedrons determines the negative charge of the skeleton, which is compensated by the charges of the univalent or bivalent cations positioned together with water molecules in the channels of the structure. The cations present in the channels are easily replaceable and are called exchange cations.

The capacity of zeolites for ion exchange without disruption of the crystal structure of the mineral is a result of the considerable inhomogeneity of the binding forces in them. For example, zeolites possess strong, mainly covalent oxygen bonds with tetrahedron cations and weak, predominantly ionic bonds between the exchange ions and the aluminum-silicon-oxygen skeleton. In addition, the presence of open voids and wide channels in their structure provides for easy occurrence of ion-exchange reactions even at a low temperature. As for the isomorphism of the tetrahedron cations (silicon, aluminum), it is realized only by synthesis or recrystallization of the zeolites [2].

The ion-exchange capacity of zeolites is one of the main parameters characterizing their sorption and technological properties. The maximum cation exchange capacity is determined by the charge of the anion skeleton (the number of aluminum atoms substituted for silicon atoms in the tetrahedrons) [3].

We studied zeolite from the Kholinskoe Deposit. The predominant mineral in the productive stratum of the deposit is clinoptilolite, $(Na, K)_4CaAl_6Si_{30}O_{72} \cdot 24H_2O$; its average content in the rock is 60% (here and below in mass fractions), in some regions its concentration attains 93 – 95%. We prepared ceramic pigments from a technological sample with 93% clinoptilolite and a low content of coloring oxides. The chemical composition of the zeolite sample was represented by 67.00% SiO_2, 12.83% Al_2O_3, 0.51% Fe_2O_3, 1.20% CaO, 1.72% Na_2O, 4.23% K_2O.

Zeolites from the Kholinskoe Deposit have a high exchange capacity. The ion exchange properties are considerably determined by the cationic nature of the raw material. The sodium form has the highest ion exchange capacity, the calcium form has the lowest. The mean content of oxides in the main functional thickness of the deposit is distributed as follows: $K_2O : Na_2O : CaO = 3.91 : 2.62 : 1.71$. Zeolite possesses a variable dicationic Na – K-form; the content of Na_2O fluctuates from 0.73 to 5.0%, that of K_2O fluctuates from 2.15 to 4.7% and that of CaO fluctuates from 0.67 to 3.18%. The values of the ion exchange capacity fluctuate from 0.46 to 2.17 meq/g. Rocks with the highest content of clinoptilolite possess the maximum capacity. They are recommended for use in ion exchange technology.

In order to obtain ceramic pigments, the batch was composed of Kholinskoe zeolite in the amount of 65 – 95% and coloring oxides of iron, manganese, chromium, and cobalt. The mineralizer and boric acid were introduced in excess of 100% in the amount of 2 – 5%. The chemical composition of the mixtures of the pigments is presented in Table 1.

The raw materials were crushed by wet milling, dried, and fired at 1000 – 1100°C. The obtained pigments were of

TABLE 1

Pigment	Mass fraction, %				
	zeolite	Fe_2O_3	MnO	Cr_2O_3	CoO
1	75 – 95	5 – 25	–	–	–
2	75 – 95	–	5 – 25	–	–
3	70 – 85	10 – 20	–	5 – 10	–
4	80 – 85	–	10 – 15	5	–
5	65 – 80	10 – 15	5 – 10	5 – 10	–
6	70	10	5 – 10	5 – 10	5

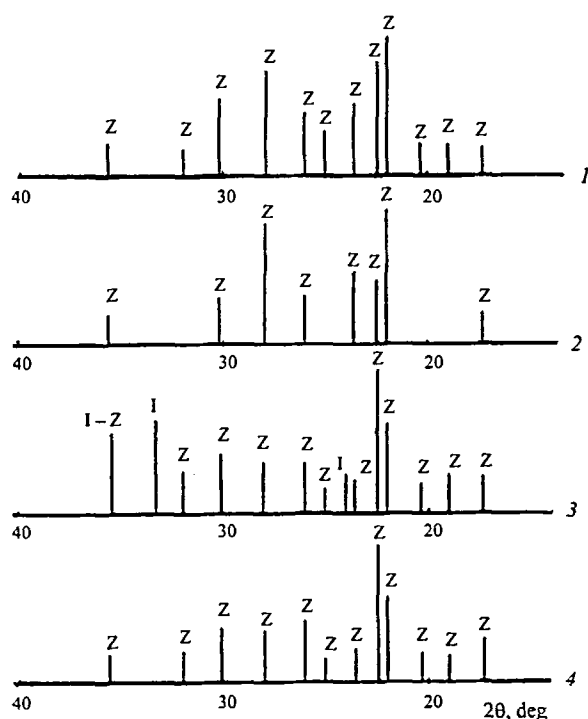[1] Tomsk Polytechnical University, Tomsk, Russia.

Fig. 1. Diffractograms of minerals and pigments after roasting at 1000°C: 1) green Kholinskoe zeolite; 2) Kholinskoe zeolite roasted at 1000°C; 3) pigment 1 (10% Fe_2O_3); 4) pigment 2 (10% MnO); Z) zeolite; 1) Fe_2O_3.

Fig. 2. Spectral reflection curves of pigments: 1) pigment 1; 2) pigment 3; 3) pigment 5; 4) pigment 4.

TABLE 2

Pigment	Pigment color at a roasting temperature of 1000°C	Color of underglaze painting. Roasting at 1030°C
1	Brick-brown	Brick
2	Dark-brown	Chocolate-brown
3	Red-brown	Olive
4	Grayish-brown	The same
5	Chocolate-brown	Brown
6	Dark-brown	Gray

TABLE 3

Pigment	Chromaticity coordinates		Dominant wavelength, nm	Hue purity, %
	x	y		
1	0.381	0.345	597	20
3	0.345	0.335	650	5
4	0.327	0.326	–	1
5	0.339	0.333	700	5

brown, gray, and olive hue. They were used for underglaze painting of earthenware (Table 2).

The x-ray analysis of the pigments was conducted using a DRON-3M diffractometer and showed that calcination of zeolite at a temperature exceeding 1000°C breaks up its structure (Fig. 1) and therefore the pigments should not be roasted at a higher temperature. The ions of bivalent metals are well "assimilated" by the crystal lattice of zeolite, which cannot be said of trivalent cations. At a 5% concentration of Fe(III), we observed diffraction peaks showing the presence of a free oxide. At 10% Fe(III), the peaks were increased considerably. It is obvious that the ionic radius allows the trivalent iron atoms to penetrate into the channels of the zeolite structure, but this disturbs the equilibrium of the electric charge and makes the isomorphic transformation impossible.

The diffractogram of the pigment with 10% manganese(II) oxide shows that the presence of oxides or manganese silicates is insignificant, which shows that the cations have been virtually fully introduced into the structure of the zeolite. The published data also prove that when cations of univalent metals are replaced by bivalent ones, the structure of the zeolite exhibits rather high exchange capacity [2].

We recorded the spectral reflection curves of the pigments (Fig. 2) using a SF-10 spectrophotometer. Curve 1 corresponding to pigment 1 indicates absorption of blue and blue-green rays, which determines the brick-red color of the pigment. Curves 2 and 3 pass smoothly from the absorption of blue and green rays to reflection of red and purple waves. Their color is close to red-brown. Dark-brown and gray-brown pigments are close to achromatic and therefore do not have well manifested reflection maxima (curve 4).
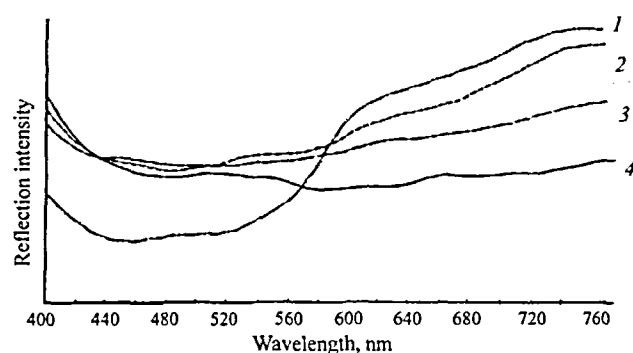
The color characteristics of the pigments are presented in Table 3.

Using a zeolite base, we can pass to the structure of anorthite and mullite with the corresponding additives. For example, on introduction of Al_2O_3 and $CaSiO_3$ wollastonite (chain) into a (Na, $K)_4CaAl_6Si_{30}O_{72} \cdot 24H_2O$ skeleton zeolite, we obtained $CaAl_2Si_2O_8$ anorthite (skeleton), and with the introduction of only Al_2O_3 we obtained $Al_6Si_2O_{13}$ mullite (chain). Taking into account the special features of the isomorphism of the trivalent cations in the zeolite structure, we should be interested in their incorporation into the crystal lattice during its restructuring in synthesis of new substances.

Our study showed that it is economically expedient to use natural zeolite for fabricating ceramic pigments. This will decrease the synthesis temperature, make production less expensive, and widen the color set of the pigments.

REFERENCES

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